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IUPAC Technical Report

Clive Bucknall*, Volker Altstädt, Dietmar Auhl, Paul Buckley, Dirk Dijkstra, Andrzej Galeski, Christoph Gögelein, Ulrich A. Handge, Jiasong He, Chen-Yang Liu, Goerg Michler, Ewa Piorkowska, Miroslav Slouf, Iakovos Vittorias and Jun Jie Wu

Structure, processing and performance of ultra-high molecular weight polyethylene (IUPAC Technical Report). Part 1: characterizing molecular weight

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Abstract: The aim of this project was to study the efficacy of current methods of quality control and quality assurance for ultra-high molecular weight polyethylene (UHMWPE) products, and find improvements where possible. Intrinsic viscosity (IV) tests were performed on three grades of polyethylene with weight average relative molar masses \overline{M}_w of about 6×10^5 , 5.0×10^6 and 9.0×10^6 . Results from three laboratories showed substantial scatter, probably because different methods were used to make and test solutions. Tensile tests were carried out to 600 % extension at 150 °C under both constant applied load and constant Hencky strain rate, on compression mouldings made by a leading manufacturer of ultra-high molecular weight polyethylene. They gave low values of \overline{M}_w , suggesting incomplete entanglement at ‘grain boundaries’ between powder particles. Results from conventional melt-rheology tests are presented, and their relevance to quality control and assurance is discussed. Attempts to calculate molecular weights from these data met with limited success because of extended relaxation times. Suggestions are made for improving international standards for IV testing of UHMWPE, by investigating the various factors that can cause significant errors, and by introducing methods for checking the homogeneity (and hence validity) of the solutions tested. Part 2 addresses characterization of crystallinity and structure. Part 3 covers mechanical properties, and Part 4 focuses on the sporadic crack propagation behaviour exhibited by all three grades of UHMWPE in fatigue tests on 10 mm thick compact tension specimens.

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Keywords: high temperature creep; intrinsic viscosity; IUPAC Polymer Division; molecular weight; quality assurance; quality control; UHMWPE.

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1 Introduction

This is the first of four reports from IUPAC Sub-Committee 4.2.1: *Structure and Properties of Commercial Polymers*, which in 2010 set up a Task Group to evaluate the effectiveness of available methods of quality control (QC) and quality assurance (QA) of ultra-high molecular weight polyethylene (UHMWPE) mouldings and to find improvements where possible. This was seen as an important investigation, because prosthetic hip and knee joints are among the most demanding applications of synthetic polymers and UHMWPE is the polymer of choice for this purpose: it is biocompatible, durable, and has robust mechanical properties. In this context, the term ‘ultra-high’ indicates a weight average relative molar mass, \overline{M}_w , greater than 10^6 . In practice, the minimum \overline{M}_w for orthopaedic grades of polyethylene (PE) is about 5×10^6 , which for linear PE means that chains have a contour length of at least 45 μm . The authors note that the more familiar and historical name of relative molecular mass is ‘molecular weight’, which features in the title of this series of reports. That name will be used throughout this series, except where numerical values are involved. Because it is impossible to process materials with such large molecules using conventional injection moulding or screw extrusion, reactor powder (fine particulate material obtained directly from the polymerization plant) is usually either ram-extruded or compression moulded under elevated pressure over extended periods of time to allow adequate levels of reptation to take place across inter-particle boundaries. Relaxation times can be reduced by raising processing temperatures, but this option has strict limits. Thermally induced chain scission must be avoided as much as possible. A related problem is that high pressures raise melting points and therefore narrow the processing window. The effect of temperature on relaxation times is less pronounced in PE than it is in other thermoplastics, because of its high crystallinity and low glass transition temperature T_g .

The UHMWPE Biomaterials Handbook covers a wide range of topics related to UHMWPE-based prostheses, ranging from polymerization to *in vivo* performance [1]. Orthopaedic implants offer great benefits to patients by relieving pain and increasing mobility, but they have a limited lifespan even under the most favourable conditions. The increasing number of treatments and the demand for implants from younger, more active patients have stimulated research to ensure a high level of performance and durability [1, 2].

Unfortunately, medical implants do not come with a guarantee of lifelong satisfaction. Historically, reported rates of recall have been about 1 % per year over the first 10 years, for reasons related to the condition of the patient, the standard of the surgery, or the quality of the implant. Records show that problems occur much more frequently over the following 10 years. Excessive wear has been the principal cause of implant-related failures, and efforts to combat this problem led in 1998 to the clinical introduction of highly crosslinked UHMWPE in place of the conventionally processed polymer. This development has its limitations (in particular, resistance to fatigue

Table 1: Laboratories contributing experimental data with two-letter codes, which are used to identify their contributions throughout this series of reports.

Laboratory	Code	Participants
Chinese Academy of Sciences	CA	Jiasong He, Chen-Yang Liu
Czech Institute of Macromolecular Chemistry	CZ	Miroslav Slouf
Durham University	DU	Jun Jie Wu
Helmholtz-Zentrum Geesthacht	HG	Ulrich A. Handge
LyondellBasell	LB	Iakovos Vittorias
Martin-Luther University	ML	Goerg Michler
Oxford University	OU	Paul Buckley
Centre of Molecular and Macromolecular Studies Polish Academy of Sciences	PA	Andrzej Galeski, Ewa Piorkowska
University of Bayreuth	UB	Volker Altstadt

crack propagation is reduced), but it has generally proved to be beneficial; technological advances of a similar kind hold out the promise of further increasing the lifespan of orthopaedic implants in the future.

It is important that implants conform to the highest possible quality standards. These are generally achieved by applying two procedures: QA, which provides confidence that quality requirements will be fulfilled; and QC, which ensures that standards are maintained in manufactured products. Applying QA and QC to ordinary general-purpose grades of PE is straightforward. Molecular weight distributions are determined routinely using size exclusion chromatography (SEC), rheological properties of molten samples are characterized over an appropriate range of temperatures and strain rates, and the data are used to model flow behaviour during moulding. If standard design and operating procedures are applied properly, failures due to moulding defects can be eliminated. However, none of these QA procedures is applicable to orthopaedic grades of PE. One difficulty is that gels consisting of persistently entangled long chains cause severe problems in SEC by clogging the columns. Another is that sintering is unable to eliminate grain-boundary ‘fusion defects’ completely. In extreme cases, these defects take the form of voids, but the majority are simply interfaces where consolidation is less than perfect. In response to these challenges, IUPAC Subcommittee 4.2.1 *Structure and Properties of Commercial Polymers* initiated this research project in 2010, with the aim of developing improved methods for characterizing UHMWPE mouldings, and hence improving QA procedures for hip and knee prostheses. Table 1 lists the laboratories and participants providing experimental data in support of this project, along with their two-letter identifying codes.

Because the relative molar mass \overline{M}_w of PE06 is below 10^6 , it should strictly be classed as HMWPE rather than UHMWPE (1). However, in the present context, it is convenient to apply the term UHMWPE to PE06 when discussing the three polymers collectively.

2 Experiments and results

2.1 Materials

In 2009–2010, a leading manufacturer of UHMWPE (identified in this report by the code letters PM) provided three grades of powder, specifically for this project, as large batches with \overline{M}_w approximately 0.6×10^6 , 5×10^6 , and 9×10^6 . They were code named PE06, PE5, and PE9 respectively. The molecular weights quoted are based on intrinsic viscosity (IV) measurements made on solutions prepared from reactor powder. The polymer manufacturer (PM) also prepared compression-moulded plaques of various thicknesses from each batch of UHMWPE in response to requests from project participants.

2.2 Solution-based measurements

Vittorias (LB in Table 1) was able to prepare gel-free solutions of PE06 from reactor powder and determine its molecular weight distribution using SEC. The results, rounded to two significant digits, are presented in

Table 2, where \overline{M}_n , the number-average relative molar mass, is the arithmetic mean of the molar mass distribution and \overline{M}_v , the viscosity-average relative molar mass, is based on earlier studies of the relationship between measured intrinsic viscosities and molecular weight distributions in PE. \overline{M}_w is the weight-average relative molar mass and \overline{M}_z is the z-average relative molar mass. The differences between the three mathematically-defined averages, and also \overline{M}_v , are shown most clearly in the following definitions:

$$\overline{M}_n = \sum N_i M_i / \sum N_i \quad (1)$$

$$\overline{M}_w = \sum N_i M_i^2 / \sum N_i M_i \quad (2)$$

$$\overline{M}_z = \sum N_i M_i^3 / \sum N_i M_i^2 \quad (3)$$

$$\overline{M}_v = \left[\sum N_i M_i^{1+a} / \sum N_i \right]^{1/a} \quad (4)$$

where the magnitude of a is determined by making experimental measurements. The ASTM standard [3] recommends the Mark–Houwink equation for converting IV $[\eta]$ into viscosity average molecular weight, \overline{M}_v , as follows:

$$\overline{M}_v = 53700 \times \left(\frac{[\eta]}{\text{dL g}^{-1}} \right)^{1.37} \quad (5)$$

By contrast, the European standard [4] uses the Margolies equation:

$$\overline{M}_v = 53700 \times \left(\frac{[\eta]}{\text{dL g}^{-1}} \right)^{1.49} \quad (6)$$

Table 2 shows that the viscosity average \overline{M}_v , described by Eq. 5, is similar in magnitude to \overline{M}_w .

SEC is not a viable option for PE5 and PE9, because neither of these polymers is sufficiently soluble in any solvent. Even at low concentrations, UHMWPE gels clog the separation columns. They also deplete the upper end of the molecular weight distribution. For these reasons, even when SEC data can be obtained, they are often disputed. An additional problem is that exceedingly long PE chains tend to crystallize in cooler sections of the chromatography equipment. Nevertheless, Talebi *et al.* have shown that it is possible to use SEC to make valid measurements of molecular weight distributions in UHMWPE, provided the polymerization process is carefully designed to avoid the formation of entanglements [5]. Using homogeneous catalysts and low-temperature polymerization conditions, they produced ‘monomolecular crystals’ which were fully soluble in 1,2,4-trichlorobenzene. When the resulting solutions were injected at 140 °C into high-temperature chromatography equipment, they produced reproducible relative molar mass distributions extending to 11×10^6 . Such high levels of solubility are lost if the reactor powder is heated to a temperature at which reptation takes place and entanglements are formed. Consequently, it is impossible to make valid SEC measurements on melt-processed UHMWPE.

Fortunately, there are other ways of characterizing the molecular weights of PE samples. They are much less powerful, but potentially helpful for QA and QC purposes. Commercially-produced reactor powders are usually sufficiently soluble in decalin to permit reproducible and valid measurements of IV, symbol $[\eta]$, see IUPAC Recommendations [6], provided that adequate precautions are taken. In some cases, it is also possible to perform IV tests on solutions made from compression-moulded or extruded samples. However, processing inevitably results in increased entanglement and the validity of the results is therefore questionable.

Table 2: Molecular weight averages for PE06, obtained using size exclusion chromatography (LB). Combined standard uncertainty $u_c \approx 5\%$.

$\overline{M}_n \times 10^{-6}$	$\overline{M}_v \times 10^{-6}$	$\overline{M}_w \times 10^{-6}$	$\overline{M}_z \times 10^{-6}$
0.023	0.54	0.59	3.9

Both American and European standards specify that $[\eta]$ should be measured at 135 °C, using an Ubbelohde capillary viscometer. For an IV of 20 dL g⁻¹, the viscosity average molecular weights, \bar{M}_v , that are obtained from Eqs. 5 and 6 differ by approximately 43 %. These equations are valid only for solutions in decalin (decahydronaphthalene). Because decalin is toxic, it is necessary to use specialised (and rather expensive) equipment to handle this solvent. Other solvents can be used to measure intrinsic viscosity, but they require different conversion factors.

In the present project, a group led by Liu (CA) made IV measurements on all three grades of UHMWPE by dissolving samples of reactor powder in Finavestane A360B (a pharmaceutical-grade oil consisting of linear alkanes) at mass concentrations between 0.03 and 0.07 g dL⁻¹. They measured specific viscosities $[\eta]$ at 150 °C, using a TA Instruments AR-2000ex concentric cylinder rheometer, and employed the following equation to calculate \bar{M}_v :

$$\bar{M}_v = 120\,000 \times \left(\frac{[\eta]}{\text{dL g}^{-1}} \right)^{1.67} \quad (7)$$

Two of the commercial laboratories involved in this project (codes PM and LB, Table 1) were equipped to handle potentially toxic liquids at elevated temperatures and follow the standard procedure for measuring intrinsic viscosity. A group led by Vittorias (code LB, Table 1) dissolved 15 mg samples of HMWPE and UHMWPE values in 300 mL decalin, added 0.25 wt. % of Irganox 1010 antioxidant as a stabilizer, heated the vials to 165 °C, and allowed the solutions to equilibrate over 6 h, with gentle shaking. They then made solution viscosity measurements at 135 °C in an Ubbelohde capillary viscometer. The PM followed a similar procedure, but, in accordance with ASTM Standard D4020, used stirring rather than shaking to prepare the solutions [3]. The results obtained from IV tests by the three laboratories are presented in Tables 3 and 4. They show substantial discrepancies, for reasons that are unclear. The factors that might be responsible are reviewed in the Section 3.

Liu (code CA, Table 1) also made IV measurements on samples cut from compression-moulded PE06 sheet, which gave $[\eta]$ of 2.1 dL g⁻¹ and \bar{M}_v of 0.41×10^6 . These reduced values support the comment made earlier, that entangled gels deplete the upper end of the molecular weight distribution.

Table 3: Intrinsic viscosities $[\eta]$ in Finavestane (code CA in Table 1), and in decalin (codes PM and LB, Table 1). Uncertainty is debatable – see text.

Lab.	$[\eta]/(\text{dL g}^{-1})$		
	PE06	PE5	PE9
CA	2.9	8.5	12.5
LB	3.1	25.9	50.2
PM	5.5	20.1	30.0

Table 4: Calculated values of \bar{M}_v and \bar{M}_w for PE06, PE5 and PE9 obtained by three laboratories using a range of experimental techniques and test temperatures θ . Uncertainty is debatable – see text.

Lab. code	Test	$\theta/^\circ\text{C}$	PE06		PE5		PE9	
			$\bar{M}_v \times 10^{-6}$	$\bar{M}_w \times 10^{-6}$	$\bar{M}_v \times 10^{-6}$	$\bar{M}_w \times 10^{-6}$	$\bar{M}_v \times 10^{-6}$	$\bar{M}_w \times 10^{-6}$
CA	IV Finavestane	150	0.69	–	4.3	–	8.1	–
CA	Constant σ	150	–	–	–	3.8	–	5.6
CA	Constant $\dot{\epsilon}_H$	150	–	–	–	4.2	–	5.6
LB	SEC	135	0.54	0.59	–	–	–	–
LB	IV Decalin	135	0.29	–	6.9	–	18.4	–
PM	IV Decalin	135	0.70	–	5.7	–	8.5	–

2.3 Tensile testing to large strains

In addition to the results from IV tests, Table 4 contains two sets of molecular weight data obtained from uniaxial tensile tests at 150 °C. Although PMs rely heavily on size-exclusion chromatography to characterize their products wherever possible, melt rheology is widely used as an alternative source of information about molecular weight. Available methods range from simple melt-flow index testing to the complete characterization of relaxation spectra. In the case of UHMWPE, it is possible (at least in principle) to determine \bar{M}_w by making use of its quasi-solid behaviour immediately above the melting point, following ISO standard 11542-2 [4]. Accordingly, a group led by Liu made measurements on tensile bars cut from PE5 and PE9 compression mouldings. Tests were carried out on six identical specimens of each material, each of which was clamped at the upper end and loaded with a different weight at the lower end. The bars were immersed in silicone oil at 150 °C, brought to thermal equilibrium, and subjected to creep tests in accordance with the ASTM standard [3] at stresses ranging from 0.1 to 0.9 MPa. In this context, the applied stress specified is the engineering stress (load/original area). The bars were 1 mm thick, with parallel gauge sections 4 mm long and 5 mm wide. The standard describes a method for determining the specific elongational stresses required to produce extensions of 600 % in 10 min. However, in the present study the chosen stresses were lower than those specified by ASTM, and the duration of the test was much longer. It was impossible to carry out similar tests on PE06, because specimens extended 600 % in less than 10 min under the minimum stress of 0.1 MPa.

Data on creep strain $\varepsilon(t)$ and applied tensile stress τ_0 were used to calculate the tensile creep compliance $D(t)$, where:

$$D(t) = \frac{\varepsilon(t)}{\tau_0} \quad (8)$$

In the most general case, $D(t)$ can be expressed as the sum of three terms:

$$D(t) = D_0 + D_{\text{rec}}(t) + t/\eta_{\text{nrec}} \quad (9)$$

where D_0 is the initial elastic compliance; D_{rec} is the recoverable, time-dependent, viscoelastic response; and t/η_{nrec} is the non-recoverable tensile creep compliance. As shown in Fig. 1, these terms represent contributions from (a) a linear (Hookean) spring, (b) a Hookean spring in parallel with a simple (constant viscosity) dashpot, and (c) a simple dashpot (Burgers model).

Data on $D(t)$ were used to determine $\eta_{0,e}$, the steady-state extensional viscosity in the linear viscoelastic regime, which is higher than the zero shear rate viscosity η_0 by a factor of three. The value of $\eta_{0,e}$ (which is equal to η_{nrec} in the Burgers model) is defined as the limiting value of $t/D(t)$, as t tends to infinity and the applied stress τ_0 tends to zero:

$$\eta_{0,e} = 3\eta_0 = \lim_{\substack{t \rightarrow \infty \\ \tau_0 \rightarrow 0}} \frac{t}{D(t)} \quad (10)$$

The application of this equation is illustrated in Fig. 2, which shows the calculated viscosity reaching a limit after 10 000 s. For PE5, $\eta_{0,e}$ is 1.4 GPa s. For PE9, $\eta_{0,e}$ is 5.2 GPa s. These results convert to a \bar{M}_w of 3.8×10^6 for PE5 and a \bar{M}_w of 5.6×10^6 for PE9.

Liu's group also used another, slightly different method to measure \bar{M}_w , in which 5 mm long, 1 mm thick tensile specimens with a width of 4 mm in the central section were subjected to tensile stretching at a constant Hencky strain rate $\dot{\varepsilon}_H$, where

$$\dot{\varepsilon}_H = \frac{1}{L(t)} \frac{dL(t)}{dt} \quad (11)$$

and $L(t)$ is the length of the specimen at time t . Tests were conducted at 150 °C in a nitrogen atmosphere at a strain rate of 0.0001 s^{-1} . The time-dependent elongational viscosity, η_e , was then expressed as the ratio of true stress, $\tau(t)$, to Hencky strain rate:

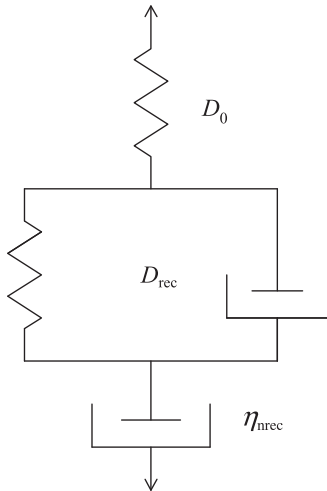


Fig. 1: Schematic diagram showing four-element Burgers model used to interpret creep data.

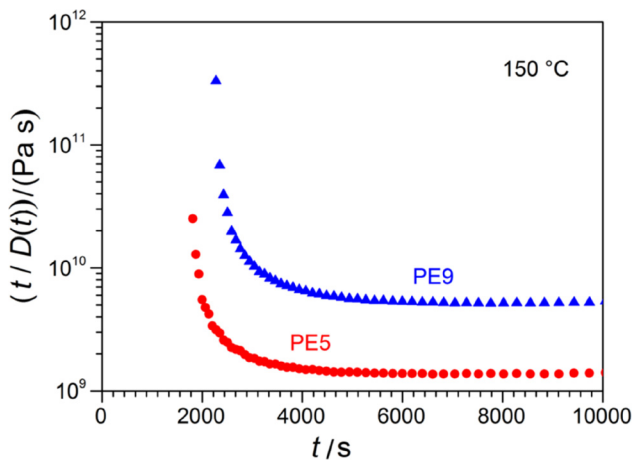


Fig. 2: Curves used to determine limiting viscosities for PE5 and PE 9. Data of Liu (code CA, Table 1).

$$\eta_e = \frac{\tau(t)}{\dot{\epsilon}_H} = \frac{F(t)}{A(t)\dot{\epsilon}_H} \quad (12)$$

where $F(t)$ is the applied force and $A(t)$ is the cross-sectional area of the specimen at time t .

Figure 3 shows results for PE5 and PE9 at a constant Hencky strain rate of 0.0001 s^{-1} . It is clear from the force-time curves that there is a marked difference in deformation behaviour between the two materials. As the specimens were 1 mm thick and 4 mm wide, PE5 reached a maximum stress of 0.13 MPa, while the maximum for PE9 was 0.25 MPa. By contrast, stress-strain curves obtained from tensile tests at 23°C show very little difference between PE5 and PE9 — see Part 3 in this series. The elongational viscosity curves in Fig. 3 do not extend far enough to define limiting values accurately, but the extrapolation of the two curves beyond t of 10 000 s suggests an approximate limit at an $\eta_{0,e}$ of 1.8 GPa s for PE5 and of 5.0 GPa s for PE9. Applying the following equation to these data:

$$\frac{\eta_{0,e}}{\text{Pa s}} = 5.8 \times 10^{-14} \times \overline{M}_w^{3.4} \quad (13)$$

The estimated values of \overline{M}_w are 4.2×10^6 for PE5 and 5.5×10^6 for PE9. These calculations are based on the assumption that the elastic behaviour of both polymers is linear and that their viscosities are able to reach a limit. Finally, it should be noted that values for \overline{M}_v can also be obtained from elongational rheometry data, as specified in DIN standard 53 493 [7].

2.4 Oscillatory shear tests on melts

To obtain worthwhile information about distributions of molecular weight from the relaxation time spectra of UHMWPE melts, it is necessary to make measurements of storage and loss moduli G' and G'' over a wide range of frequencies. Ideally, these should extend to frequencies that are low enough, or relaxation times that are long enough, for G' to fall below G'' in what is called the terminal regime, with characteristic slopes of unity for G'' and of two for G' on a double-logarithmic scale. This is difficult to achieve when \bar{M}_w is greater than 3×10^6 . To minimise thermal degradation, temperatures should preferably be between 140 °C and 160 °C, which are above the melting point of UHMWPE. However, since the time-temperature superposition principle requires relaxation times to shift with temperature, the range of frequencies accessible to rheometers does not extend to frequencies that are low enough to cover the whole spectrum. Raising the temperature above this range for an extended period not only reduces relaxation times, but also increases the probability of undesirable structural changes, notably chain scission.

For this reason, Vittorias (code LB, Table 1) carried out oscillatory shear tests at 210 °C on discs about 1 mm thick and 25 mm in diameter, which were prepared by compression moulding reactor powder mixed with 0.25 % by weight of Irganox 1010 stabilizer. Mouldings were held for 10 min at 200 °C under a pressure of 200 bar. As both PE5 and PE9 samples generated significant normal forces when first inserted between the rheometer plates, trials were conducted with various specimen thicknesses and preparation procedures, involving different conditioning times, temperatures, and pressures. These showed that preheating for up to 1 h at 210 °C was necessary to obtain a stable sample, while the stabilizer prevented significant damage involving degradation or crosslinking. The results from tests on the stabilised specimens are summarised in Fig. 4. In contrast to Fig. 3, the curves for PE5 and PE9 are close together, with a small separation only at low frequencies. There is a more substantial difference in rheological behaviour between PE06 and the two UHMWPE grades. However, none of the curves extends into the region where the magnitude of the complex viscosity modulus $|\eta^*|$ is independent of angular frequency ω . Consequently, it is not possible to define a viscosity at zero shear rate in the accessible frequency range.

Liu used a rotational rheometer to characterize the viscoelastic behaviour of PE06, PE5, and PE9 at 190 °C. The results are presented in Fig. 5, where the dashed line at 2 MPa defines the plateau modulus of PE at high frequencies. When the data in Fig. 5 are converted to complex viscosities, they are in good agreement with the curves in Fig. 4. Handge (code HG, Table 1) employed rotational rheometry to analyse the viscoelastic properties of the three UHMWPE grades using an MCR 502 rheometer (Anton Paar GmbH, Graz, Austria). This was fitted with 25 mm diameter parallel plates to make oscillatory shear measurements on discs with diameters of 20 mm and thicknesses of 2 mm, which were cut from compression-moulded plaques. They were first dried at 35 °C under vacuum for at least 12 h. Tests were then carried out in a nitrogen atmosphere. When samples were inserted into the rheometer, care was taken that normal forces (resulting from both thermal expansion and

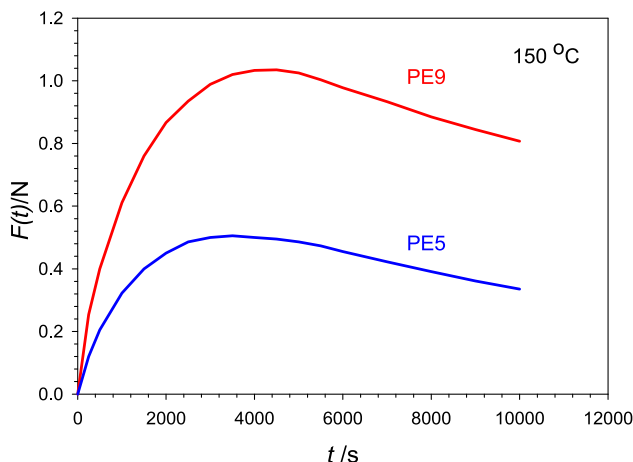


Fig. 3: Force $F(t)$ vs. time t curves for PE5 and PE9 at 150 °C, at a Hencky strain rate of 0.0001 s^{-1} . Data of Liu (code CA, Table 1).

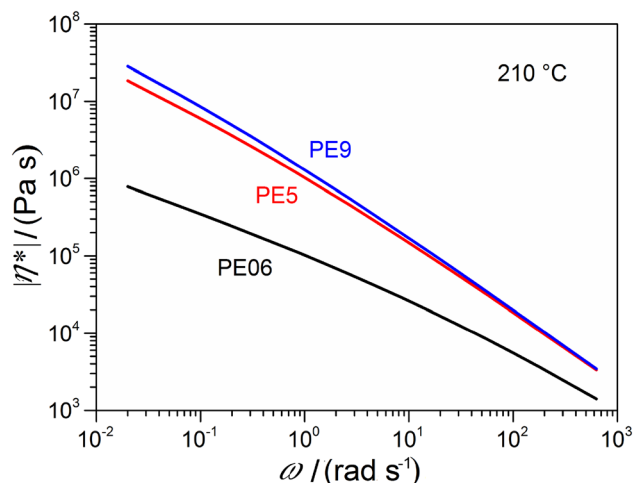


Fig. 4: Relationship between complex viscosity modulus $|\eta^*|$ and angular frequency ω for PE06, PE5 and PE9 at 210 °C. Data of Vittorias (code LB, Table 1).

slight compression of the sample) were minimized. The stability of each material was first tested during 3-h time sweeps at 150 °C and 190 °C at a fixed angular velocity ω of 0.1 rad s⁻¹ and shear amplitude γ_0 of 5 %. Thermal expansion coefficients were used to calculate specimen diameters at the test temperature, following the method used by Sentmanat *et al.* [9]. Figure 6 shows that the dynamic moduli G' and G'' of all three grades of UHMWPE were independent of shear strain amplitude when γ_0 was increased from 1 to 10 %. Figure 7a shows that the storage modulus G' remained independent of time in PE5 and PE9 throughout the sweep at both temperatures. However, in Fig. 7b, the storage modulus of PE06 shows a moderate increase from 44 to 54 kPa at 150 °C, as well as a larger increase from 52 to 70 kPa at 190 °C.

2.5 Creep and recovery under shear

Another method for studying the flow behaviour of polymers over long periods of time is the creep recovery experiment [10]. In order to obtain data on PE06, PE5, and PE9 in the linear viscoelastic regime, creep recovery experiments were performed in shear (code HG, Table 1) using an MCR 502 rotational rheometer with plate-plate geometry. All tests were carried out at 150 °C in a nitrogen atmosphere over a creep time t_{\max} of 10 000 s. The applied shear stress, $\tau_{xy,0}$, was set at 500 Pa, which is much smaller than the stresses applied in tensile creep tests and belongs to the linear regime. A stress of 500 Pa was chosen after analysing amplitude sweeps in the range 10 to 1000 Pa at an angular frequency of 10 rad s⁻¹. In the creep recovery experiments, shear creep compliance, $J(t) = \gamma(t)/\tau_{xy,0}$, was determined, where $\gamma(t)$ is the shear strain at time t . After the applied stress was

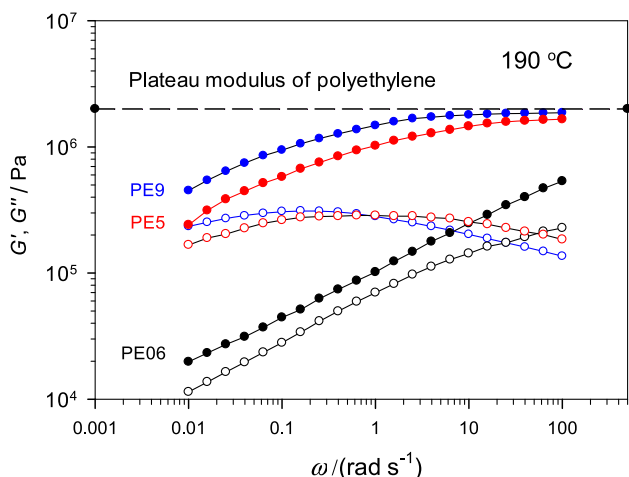


Fig. 5: Storage modulus G' (closed symbols) and loss modulus G'' (open symbols) vs. angular frequency from tests at 190 °C. Data of Liu (CA). Dashed horizontal line defines plateau modulus of PE at high frequencies [8].

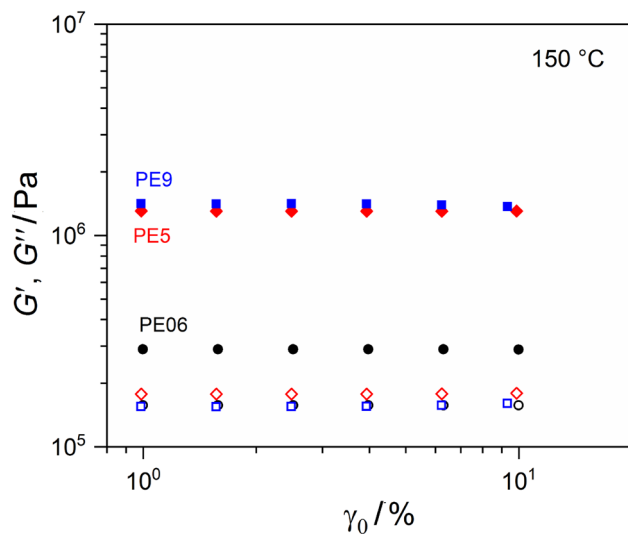


Fig. 6: Effects of shear amplitude γ_0 on dynamic moduli G' (closed symbols) and G'' (open symbols) at 150 °C. Data of Handge (code HG, Table 1).

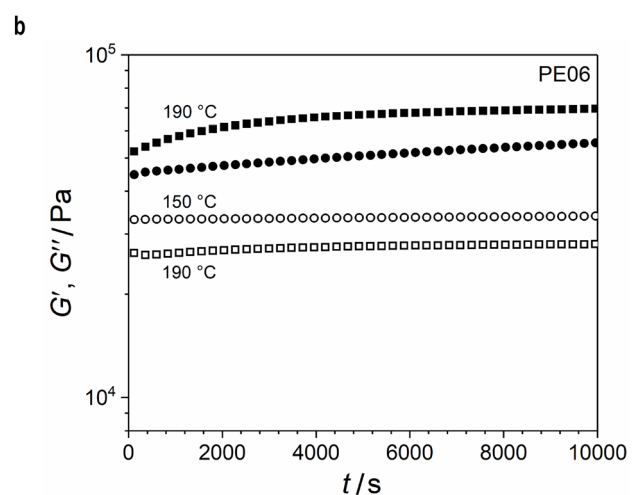
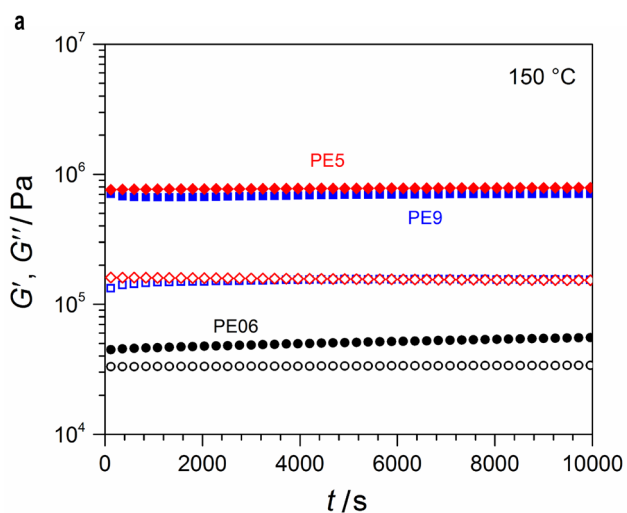


Fig. 7: (a). Thermal stability tests at 150 °C on PE06, PE5 and PE9 at an angular frequency ω of 0.1 rad s⁻¹; Storage modulus G' (closed symbols) and loss modulus G'' (open symbols) vs. time t . (Handge, code HG, Table 1). (b). Thermal stability of PE06. Storage modulus G' (closed symbols) and loss modulus G'' (open symbols) vs. time t , circles 150 °C; squares 190 °C. (Handge, code HG, Table 1).

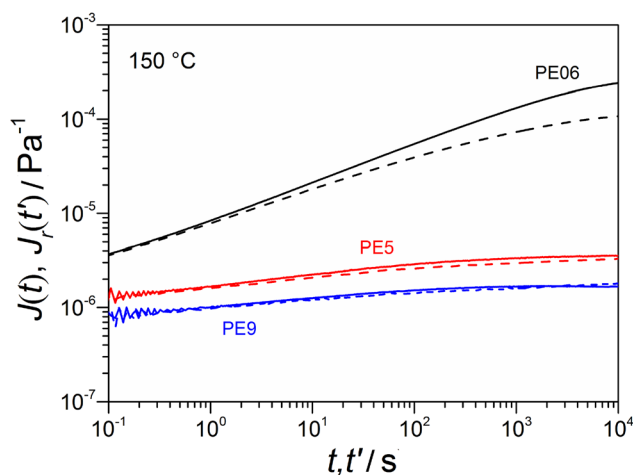


Fig. 8: Creep compliance $J(t)$ (continuous curves) and recovered creep compliance $J_r(t')$ (short dashes) vs. time determined in shear experiments at 150 °C with $\tau_{xy,0}$ of 500 Pa. Handge (code HG, Table 1).

removed, a new time scale ($t' = t - t_{\max}$) was employed, and the recovered creep compliance $J_r(t')$ was recorded, where

$$J_r(t') = \frac{\gamma_{\max} - \gamma(t')}{\tau_{xy,0}} \quad (14)$$

and γ_{\max} is the shear strain attained at time $t = t_{\max}$.

Results from these experiments are presented in Fig. 8. They show clearly that the terminal regime, which has a slope of unity, is not achieved in any of the UHMWPE grades selected for this study, and they demonstrate that the regime of Newtonian flow cannot be reached within a reasonable experimental time period. Furthermore, the recovered compliance, $J_r(t')$, is significantly smaller than the creep compliance, $J(t)$, in PE06, whereas $J(t)$ is equal to $J_r(t')$ within experimental scatter in PE5 and PE9. This result shows that fully elastic (reversible) behaviour is achieved only in the two ultra-high molecular weight grades. The elasticity of PE5 and PE9 is also indicated by the ‘creep-ringing’ effect shown in Fig. 8, where the compliance oscillates during the first 10th of a second.

3 Discussion

The standard methods for measuring the molecular weights of thermoplastics were not designed for polymers with extremely long chains. Their limitations are highlighted in this report. They are most apparent in the case of SEC, which depends for its viability on complete solubility of the sample, which is hard to achieve. However, difficulties are also encountered in the determination of intrinsic viscosity, where it is possible to make measurements on UHMWPE solutions, but the validity of the data obtained from these measurements depends critically on the history of the original sample, the techniques used to prepare solutions, and the test procedure.

Experiments on solutions prepared from commercially produced UHMWPE reactor powder show that they invariably contain some entanglement gels, which not only distort SEC data by preferentially depleting the upper end of the molecular weight distribution, but also tend to clog the chromatography columns, rendering them unusable. Talebi and co-workers have demonstrated that it is possible to use SEC for characterizing UHMWPE, but only when extreme care is taken to avoid the formation of entanglements during polymerization [5]. Furthermore, it is well known in the industry that gel contents increase dramatically in samples that have been melt-processed. In light of this experience, task group members decided to exclude SEC from the main experimental program. One exception was made; a single SEC test was carried out on PE06, which has a \overline{M}_w well below 10⁶, and is therefore not a true UHMWPE.

In response to the limitations of SEC, some manufacturers use IV measurements to measure molecular weights, following ASTM or ISO standards [3, 4]. As noted earlier, the application of IV-based test methods to UHMWPE is not without its difficulties, but these can be minimised by taking great care during the preparation of solutions, to ensure that the concentration of persistently entangled molecules is as low as possible. Factors known to affect the gel content include the concentration of UHMWPE in the initial solution and the method of agitation during its preparation, but there is little (if any) published information on the subject. The ASTM standard recommends stirring [3], while ISO standard specifies shaking [4], which is thought to minimise shear-induced chain scission.

The \overline{M}_v data presented in Table 4 show good agreement between different participants in some areas and large discrepancies in others. In particular, Vittorias (code LB, Table 1) obtained a very low value for PE06 and an extremely high value for PE9 from IV tests, for reasons that are far from clear. Since the method for measuring IV is quite simple, and unlikely to pose significant problems, the observed variations presumably arise from differences in the procedures used in preparing the required solutions. Further investigation of probable causes is beyond the scope of the present investigation. The data in Table 4 clearly demonstrate the problems associated with IV testing.

Currently, international standards for IV testing of UHMWPE make no mention of its limited solubility, or of possible changes taking place during moulding, as a result of thermal degradation. There is no guidance in the standards on how to minimise the content of insoluble gel when making a solution, or on possible methods for assessing gel content and thus ensuring that test results are valid. Some basic principles are well known within the industry: solutions should always be made from reactor powder; concentrations in initial solutions should be kept as low as possible, in order to minimise entanglement; and stirrer speeds should be kept low, to minimise chain scission. Unfortunately, there is no procedure for determining whether a particular solution is able to provide valid data in IV tests. Manufacturers simply have to develop methods that give consistent results over an extended period of time, and use those methods for QC purposes. International standards could be improved by adding some guidance on possible sources of error in IV testing of UHMWPE, just as standards for fracture mechanics testing always specify thicknesses greater than a calculated minimum for test specimens to ensure the validity of fracture toughness data. It is more difficult to formulate criteria for the validity of IV test solutions, but any soundly-based guidance would be better than none. It might be possible, for example, to use turbidity measurements to detect gels.

There is a further problem with \overline{M}_v data obtained from IV tests on UHMWPE. Even when they are accurate, they are not necessarily reliable indicators of product performance, because that is determined largely by the polymer's rheological properties in the melt, and hence by both \overline{M}_v and molecular weight distribution. During a production run, it is possible (at least in principle) to have fluctuations in molecular weight distribution, while \overline{M}_v remains essentially constant. Consequently, information obtained from simple melt flow index testing is often more useful, for QA and QC purposes, than IV data. Discussions with members of SC4.2.1 who have experience in the field of UHMWPE production indicate that a number of polymer producers rely more on melt rheology than \overline{M}_v measurements to monitor their products.

In the present study, attempts to characterize molecular weights using conventional melt rheology tests proved largely unsuccessful. Ideally, testing would extend over a range of times or frequencies that is sufficiently wide to characterize the entire molecular weight distribution. However, at 150 °C, just above the melting point, relaxation times are extremely long and thermal degradation can become a significant issue during extended tests. For the same reasons, there are limits on the extent to which the temperature can be raised to accelerate relaxation.

The most promising rheological results are the elongational viscosity data shown in Figs. 2 and 3. Again, concern about thermal degradation led to restrictions on this experimental work. The tests extended over 3 h, which was not sufficient to enable limiting values to be determined with any accuracy. On the other hand, these tests demonstrate clear differences between PE5 and PE9, to a degree that other rheological tests do not. In contrast to applied-shear tests, melt elongation is generally associated with large strains, at which the response of the material is nonlinear. Values of \overline{M}_w obtained from tests at both constant engineering stress and constant Hencky strain rate were approximately 4.0 MPa for PE5 and 5.6 MPa for PE9. Since this study was

aimed primarily at assessing and improving QA and QC procedures, rather than at the accurate characterization of molecular weight averages and distributions, there is a case for developing new tests based on elongational rheology to monitor quality. As part of that study, the possibility of extending tests at 150 °C beyond 3 h should be explored, using samples containing Irganox 1010 or a comparable stabilizer.

Potentially, elongational rheometry could also provide information about the mechanical integrity of mouldings, where a 100 % integrity rating indicates the complete absence of fusion defects. This possibility is suggested by differences between the calculated values of \overline{M}_w for PE5 and PE9 obtained from tensile rheometry and the corresponding \overline{M}_v data presented in Table 4. Overall, the \overline{M}_v values are higher than the \overline{M}_w values, as indicated in Table 1, although the opposite should be true. This anomaly could be due simply to experimental error, but it is probably of real significance. Calculations of \overline{M}_w using Eq. 10 are based on the assumption that the sample has reached thermodynamic equilibrium; in other words (neglecting energetic contributions to the Helmholtz energy), the entropy of mixing between chains originating from different powder particles has reached a maximum. That is a reasonable assumption when \overline{M}_w is below 10^5 , but not when it is well over 10^6 . It is well known that fusion defects of various kinds are present in most UHMWPE mouldings, and it follows that the levels of entanglement in and around grain boundaries must be less than optimum. Accelerated shear rates in these boundaries during tensile rheometry tests at 150 °C could account for the lower than expected values obtained for limiting zero shear rate viscosity, η_0 , and consequently the anomalously low \overline{M}_w . This hypothesis could be tested by studying the effect of sub-standard moulding conditions on creep rates in UHMWPE at temperatures immediately above the melting point. Tests at constant Hencky strain rate would be equally suitable for this purpose.

4 Conclusions

It is well known that SEC cannot be used to measure molecular weight distributions in commercial grades of UHMWPE, because solutions, however well prepared, always contain entanglement gels. These difficulties can be avoided by using IV tests, but those tests have serious limitations. Most obviously, they provide a simple viscosity average molecular weight, with no information about molecular weight distribution. Furthermore, the reproducibility of IV data from UHMWPE solutions depends critically on the experimental skills and experience of the investigator. Those who are familiar with this area are aware that the concentration of the initial solution is important. It must be high enough to define IV clearly, but not so high that it enables gels to form. Shaking or stirring at elevated temperatures must be used in preparing the solutions, but care must be taken to avoid thermally- or mechanically-induced chain scission. Among experts, opinions differ on whether shaking or stirring is the better choice. These issues raise questions about the suitability of IV testing as a QA or QC procedure. If the results depend so critically on the experience and manual dexterity of the investigator, they cannot be regarded as completely reliable.

Melt rheology provides an alternative approach to the characterization of the molecular weight of polymers with very long chains. The preferred procedure is to produce a complete relaxation spectrum, but frequency sweeps and creep recovery tests show that the spectra of HMWPE and UHMWPE are far too broad to achieve the terminal regime under realistic experimental conditions. Thermal degradation problems place limits on the times over which the tests can be extended and on the temperatures at which measurements can be made: 210 °C is probably near the upper limit. However, tensile melt rheology at high stresses and strains has shown promise as an alternative method for characterizing molecular weight. Tensile tests at 150 °C, at both constant applied loads and constant Hencky strain rates, have provided some interesting data that distinguish clearly between PE5 and PE9. There is a strong case for exploring the potential of these methods further by extending the temperature range and adjusting other experimental conditions.

Molecular weight is not the only factor affecting the performance of products made from UHMWPE. Crystalline structure and the quality of consolidation in the melt state are also very important. Part 2 of this series reviews data on melting, crystallization, lamellar thickness, anisotropy, and fusion defects in the compression mouldings prepared for this project. Part 3 covers a wide range of mechanical properties, including yielding in

tension and compression, hardness, and wear. Part 4, the last in this series, describes the extraordinary sporadic crack growth behaviour exhibited by PE06, PE5, and PE9 in fatigue tests on 10 mm thick compact tension specimens, and gives reasons for concluding that it is caused by incomplete consolidation during melt processing.

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References

- [1] S. M. Kurtz. *UHMWPE Biomaterials Handbook – 3rd Edition*, Elsevier, Amsterdam (2015).
- [2] P. Bracco, A. Bellare, A. Bistolfi, S. Affatato. *Materials* **10**, 791 (2017).
- [3] ASTM Standard D4020-18. *Standard Specification for Ultra-High-Molecular-Weight Polyethylene Molding and Extrusion Materials*, ASTM International, West Conshohocken, PA (2018), www.astm.org.
- [4] ISO Standard 11542-2. *Plastics. Ultra-High-Molecular-Weight Polyethylene (PE-UHMW) Moulding and Extrusion Materials. Part 2: Preparation of Test Specimens and Determination of Properties* (1998).
- [5] S. Talebi, R. Duchateaux, S. Rastogi, J. Kaschta, G. W. M. Peters, P. J. Lemstra. *Macromolecules* **43**, 2780 (2010).
- [6] R. G. Jones, J. Kahovec, R. Stepto, E. S. Wilks, M. Hess, T. Kitayama, W. Val Metanowski (Eds.), *Compendium of Polymer Terminology and Nomenclature, IUPAC Recommendations 2008*, p. 54, The Royal Society of Chemistry, Cambridge (2009).

- [7] DIN 53493. *Testing of Plastics; Determination on Flow Value of Ultra-High Molecular Weight Polyethylene*, Deutsches Institut für Normung E.V. (DIN), Berlin, Germany (1980).
- [8] P. M. Wood-Adams, J. M. Dealy, A. W. deGroot, O. D. Redwine. *Macromolecules* **33**, 7489 (2000).
- [9] M. Sentmanat, B. N. Wang, G. H. McGinley. *J. Rheol.* **49**, 585 (2005).
- [10] H. Münstedt. *J. Rheol.* **58**, 565 (2014).